Full microscopic treatment of the optical response of the Si(100) 2×1 surface

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Abstract

The optical reflection from the Si(100) 2×1 surface has been calculated, using the discrete dipole model and local polarizabilities obtained from quantum mechanical cluster calculations. Results have been compared with experimental differential reflectance (Si) and optical anisotropy measurements (Ge).

1. Introduction

The optical properties of the outermost monolayers of a crystalline substrate are significantly different from those of its bulk interior. This deviating behaviour is shown experimentally in reflectance difference (RD) and anisotropic reflection difference measurements. Most interpretations of such surface optical experiments are based on continuum models. Continuum models, however, have no direct access to the microscopic geometry of the surface. This aspect is better accounted for in a discrete model, although models of that kind, such as the discrete dipole model, require in general elaborate calculations. Using the double cell method [1, 2] the numerical effort can be reduced to manageable proportions for realistic surfaces. In the discrete dipole approach the microscopic material parameters are the local polarizabilities. We investigate in this article the possibility of calculating those local polarizabilities in a direct way. The results of this new approach will be used to calculate the optical response of the Si(100) 2×1 surface.

2. Discrete dipole theory

In a number of previous publications [1–3] we have shown that the optical response of crystalline surfaces can be found by representing the semi-infinite system by lattice planes of dipoles, where a single characteristic dipole $\mathbf{p}_i$ controls the entire behaviour of a plane i . This planewise description as such is only suited for the few outermost planes. The bulk optical response is most efficiently described by means of normal modes. In this way the discrete dipoles can be obtained directly on solution of the semi-infinite (double cell) interaction equations:

$$\|\mathbf{M}\|_{\mathbf{p}_i, v_m} = |\mathbf{E}_i, \mathcal{E}_m| \quad (1)$$

$\mathbf{M}$ is the double cell interaction matrix, v_m the strength of the m th normal mode and $\mathbf{E}_i, \mathcal{E}_m$ represent the incoming electromagnetic field. The microscopic parameters $\mathbf{p}_i, v_m$ determine the complex reflection coefficient r for an incoming electric field $\mathbf{E}_0 \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)]$ through

$$r = \frac{ik^2}{2\mathcal{S}_{ws}|k_z|} \frac{\hat{\mathbf{t}} \cdot \mathbf{P}(\mathbf{k})}{\epsilon_0 E_0} \quad (2)$$

$\hat{\mathbf{t}}$ is the polarization direction (s or p), $\mathcal{S}_{ws}$ the area of the surface unit cell and $\mathbf{P}(\mathbf{k})$ is the vector which depends on $\mathbf{p}_i, v_m$ and whose precise definition is given in ref. 1, where also the definition of the other parameters used in eqn. (2) can be found. In this derivation the previously mentioned local polarizability tensors α_i enter through the subtensor elements $\mathbf{M}_{ii}$, which obey the definition

$$\mathbf{M}_{ii} = \alpha_i^{-1} - \alpha_0^{-1} \mathbf{f}_{ii} \quad (3)$$

The $\mathbf{f}_{ii}$ are transfer tensors and α_0 is a unit of polarizability [1]. The local polarizability tensors α_i belong to a discrete (point-like) picture from the electrodynamic point of view. Quantum mechanically they have to be seen as cellular quantities. Implicitly this idea is used in the optics of single atoms, but we want to investigate whether this idea can be made useful in crystal optics as well. The crucial point is the treatment of the optical absorption. The prevailing strategy for bulk optics is to balance the energy absorbed by the electrons and the energy dissipated by the electromagnetic field according to the dielectric constant description [4]. This approach implicitly neglects the finite lifetime of excited electrons. Atomistic optical models take this finite lifetime into account, as does the GW method [5]. For this reason we start from the non-hermitian hamiltonian:

$$\tilde{H} = \frac{p^2}{2m} - e\Phi_0(\mathbf{r}) + \tilde{\Sigma} + \frac{e}{m} \mathbf{A}(\mathbf{r}, t) \cdot \mathbf{p} \quad (4)$$

where Σ is the self-energy, being zero for the ground state and complex for the excited states. Staying closely with the derivation as can be found in standard textbooks [6] and keeping in mind eqn. (4) it follows that

$$\alpha_k(\omega) = \frac{e^2}{\hbar} \sum_i \sum_f \langle \phi_i | \mathbf{r} | \phi_f \rangle_{\Omega_k} \langle \phi_i | \mathbf{r} | \phi_f \rangle_{\Omega_k}^* \tilde{F}_{if}(\omega) \quad (5a)$$

$$\tilde{F}_{if}(\omega) = \frac{2\omega_{if}(\omega_{if}^2 + \gamma_{if}^2 - \omega^2 + 2i\omega\gamma_{if})}{(\omega_{if}^2 - \gamma_{if}^2 - \omega^2)^2 + 4\omega_{if}^2\gamma_{if}^2} \quad (5b)$$

where α_k represents the local polarizability (tensor) of the k th cell (volume Ω_k). ϕ_i, ϕ_f are initial and final states and $\hbar(\omega_{if} + i\gamma_{if})$ is the energy difference between them. Further evaluation of eqns. (5) requires the expectation value of the position vector $\mathbf{r}$. Because of the type of quantum chemical cluster calculation used (AMPAC), only s and p orbitals can be taken into account. Therefore the terminating H atoms can have no optical response and have been neglected accordingly. As a result it suffices to know only the following matrix elements:

$$\langle s | \hat{\mathbf{r}}_u | p_u \rangle = \frac{1}{3}\sqrt{3} \hat{\mathbf{u}} \quad (u = x, y, z) \quad (6a)$$

$$\langle r \rangle_{20 \rightarrow 21} = -6\sqrt{3} a_0/Z \quad (6b)$$

$$\langle r \rangle_{30 \rightarrow 31} = -9\sqrt{2} a_0/Z \quad (6c)$$

We need only expressions for O (eqn. (6b)) and Si (eqn. (6c)). For the derivation of eqns. (6) we have used full hydrogen-like wavefunctions with the usual nl labelling. a_0 represents the Bohr radius and Z the effective atomic number. For this paper each cell will correspond to two atoms and its polarizability is a direct addition of two atomic contributions as in eqns. (5) and (6). A one atom–one dipole assignment has as yet never resulted in good results [3]. Calculating local polarizabilities by means of eqns. (5) and (6) has a straightforward character. It lacks the usual manipulation with Kramers–Kronig (KK) transforms (eqns. (5) build a KK pair) and yields for one energy immediately the full polarizability tensor. Moreover, it allows for characterization of parts of the system, rather than characterizing the system as a whole. This facilitates the study of surface optical phenomena.

Finally has to be mentioned which expression has been used for the ellipsometric parameters Ψ, Δ in the case of surface optics:

$$r_y/r_x = \tan(\Psi) e^{i\Delta} \quad (7)$$

$r_{y,x}$ are reflection coefficients. The y direction is parallel and the x direction perpendicular to the dimers of the clean surface. These directions remain the same on (N_2O) oxidation. The difference angles ($\delta\Psi, \delta\Delta$) are defined as $(\Psi_1, \Delta_1) - (\Psi_0, \Delta_0)$ where the index 1 refers to the surface of interest and 0 to an isotropic reference surface (Ψ, Δ defined by eqn. (7)). For theoretical

results this means that $\delta\Psi = \Psi_1 - 45^\circ$ and $\delta\Delta = \Delta_1$. Further, experimental $\delta\Psi$ have been obtained from the measured $\delta(\tan \Psi)$ through multiplication by $90/\pi$.

3. Calculations and results

We have approximated the electronic structure of the Si(100) surface by means of an AMPAC cluster calculation. For the clean 2×1 reconstructed surface we have used an Si_9H_{12} cluster and for the N_2O adsorbed surface an $\text{Si}_9\text{H}_{12}\text{O}_3$ cluster. The reconstructed surface has a square of size $a = 3.84 \text{ \AA}$ as surface unit cell. The four corner atoms of this unit cell make up the first layer of both clusters which are terminated at the bulk side by three more Si atoms at bulk positions. As a result of N_2O exposure one O atom will go and reside between two Si atoms placed on top of the first layer atoms at bulk positions [7–9]. The clean surface reconstructs by moving these two atoms towards each other and making a dimer, causing a surface unit cell of twice the unreconstructed size. For the asymmetric dimer we have used the coordinates as given in ref. 10.

For these two clusters we have calculated the local polarizabilities using the formulae given before (in units of α_0 [1]). The use of clusters to calculate the electronic structure of the surface requires correction of strengths and transition energies. Since the behaviour of the first layer already displays bulk-like characteristics, we have tuned the local polarizabilities of this layer, such that they approximate those of the bulk. Considering the onset of the bulk transition it turns out that the energies of the transitions have to be shifted downwards by 4.68 eV for the clean and by 4.6 eV for the oxidized cluster. Further we have scaled down $\langle r \rangle$ by a factor of 0.40 for the clean and 0.33 for the oxidized cluster. The γ_{if} required by the expressions (5) for α have all been chosen equal and given the constant value of 0.15 eV. First some remarks have to be made concerning the agreement between theory and experiment. Reliable experimental data for Si(100) exist only as RD spectra [11]. As yet there are no experimental anisotropic data available for this surface, but they exist for Ge(100) [9, 12]. From photoemission experiments, however, it is known that, apart from a small energy shift, the surface electronic structure of Ge(100) 2×1 comes close to that of Si(100) 2×1 . So the calculated Si(100) 2×1 ellipsometric spectra of this article will be compared with Ge(100) 2×1 measurements.

Polarizability components (xx and yy) obtained in this way are shown in Fig. 1 for the dimer of the clean cluster, as well as the (isotropic) bulk polarizability. Only imaginary parts have been shown, since they relate directly to electronic transitions. The most striking features in this figure are the two anisotropic transi-

Fig. 1. Imaginary part of the local polarizability as a function of energy for dimer (---, xx ; - · -, yy) and bulk (—).

tions in the y direction at 2.0 and 3.0 eV. The second peak at 3.0 eV involves only one pair of levels, the initial level being strongly localized at the dimer. The first transition at 2.0 eV involves predominantly three pairs of levels, each pair having at least one dimer-localized level. The two peaks contain the major electronic contribution to the subbandgap optical anisotropy. Similarly we have obtained polarizabilities for the oxidized clusters. The subbandgap transitions found there are at least one order of magnitude below the clean transitions and display hardly any anisotropy. Hence the usual subbandgap transparency assumption for oxidized Si surfaces is confirmed and results will not be shown.

The polarizabilities yield the macroscopic reflection on solution of eqn. (1). In view of the remarks made before, we assign values for the polarizability different from bulk to the outermost layer only. In this way we have calculated $\delta\Psi$ as a function of energy (Fig. 2) for the clean Si(100) 2×1 surface. The result is positive

Fig. 2. Ellipsometric difference angle $\delta\Psi = \Psi_1 - \Psi_0$ as a function of energy (see text): —, clean Si(100) 2×1 ; ---, clean Ge(100) 2×1 (experiment).

Fig. 3. Ellipsometric difference angles (a) $\delta\Psi = \Psi_1 - \Psi_0$ and (b) $\delta\Delta = \Delta_1 - \Delta_0$ as a function of energy (see text): —, N_2O -oxidized Si(100) 2×1 ; ---, N_2O -oxidized Ge(100) 2×1 (experiment).

and displays a small peak at 2.25 eV and a strong peak at 3.53 eV. Contrary to expectation the two anisotropic peaks in the polarizability have left no traces in the final result. Only the weak transition in the x direction at 2.30 eV has become effective. The second peak in $\delta\Psi$ corresponds to bulk. The only plausible explanation for the disappearance of the y peaks is a zero local field at the surface for the y direction. Comparison of the results with experiment is poor. The experimental peaks are found at energetically lower positions. This difference can be ascribed to the Si-Ge difference. The second calculated peak is too high in comparison with experiment.

Normal incidence ellipsometric results of the oxidized cluster are shown in Figs. 3(a) for $\delta\Psi$ and 3(b) for $\delta\Delta$. Both calculations correspond quite well to the measured results [9, 13]. The two peaks in $\delta\Psi$ and the corresponding structure in $\delta\Delta$ are energetically at the correct positions if we apply a shift of 0.3 eV. This is the already-mentioned Si-Ge shift. The theoretical peak heights ($\delta\Psi$) exceed the experimental heights, as is found more often for discrete dipole calculations. Fine structure is not expected to be reproduced by the experiment since it results almost for sure from the use of clusters. From all calculated results the anisotropic response of the oxidized surface corresponds best to experiment.

This does not mean that there are no problems with the oxidized surface. In Fig. 4 we have shown total reflectances R , for clean and oxidized Si(100) surfaces, as well as the Fresnel result. The clean surface results stay close to the Fresnel values (as they should) and the two can hardly be distinguished on this scale. The oxidized reflectance, however, deviates unacceptably much from its Fresnel counterpart. Nevertheless, the anisotropic results of Fig. 3 can still be correct, since anisotropic and the overall spectra behave relatively independently according to our experience.

In view of these remarks, it is not likely that the RD spectra (difference of clean and N_2O -oxidized reflec-

Fig. 4. Average reflectance R as a function of energy: —, bulk; - - -, clean Si(100) 2×1 ; - · -, N_2O -oxidized Si(100).

Fig. 5. Difference $\Delta R = R_{Cl} - R_{Ox}$ (Ox, N_2O oxidized) in reflectance as a function of energy.

tance) will be in agreement with experiment. Figure 5 shows this quantity, but the results are negative throughout, whereas the experiment is positive [11]. In order to obtain some feeling of where the model goes wrong, we have calculated reflectance differences for isolated outermost dipole monolayers of the Si(100) surfaces involved. Here we arrive at results having the correct sign (Fig. 5). Those spectra, however, are not suitable for spectroscopic interpretations, since monolayer results have an ω^2 modulation, as compared with corresponding semi-infinite calculations. The mono-

layer result points to effects in the interaction with the underlying bulk as a possible cause of mismatch. Those interactions in the perpendicular direction determine predominantly the RD spectra, but are relatively independent of interactions in the lateral (along the surface) direction, as mentioned before.

Summarizing we can say that, apart from the anisotropic ellipsometric data for the N_2O -oxidized Si(100) surface, the agreement between theory and experiment is poor. The discrete dipole calculations themselves are exact within assumptions. Usually in this type of calculation three or more layers deviating from bulk are used, but in this calculation only one monolayer has been different. For the observed discrepancies we have to question either the assumptions themselves or the procedure used to calculate the local polarizabilities. Before the first option can be investigated properly, the second option should be settled first. Indeed several short-cuts and questionable assumptions have been made for the calculation of the local polarizabilities. These shortcomings, however, are only technical; the more severe objection is that a cluster is only a poor approximation of a true surface. Full surface or slab-type electronic structures are expected to yield better results. In future work we plan to continue our research in that direction.

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